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Title: Predictions of x-ray scattering spectra in warm dense matter

Author(s): Starrett, Charles E.
Saumon, Didier
Souza, Andre N.
Perkins, David J.
Hansen, Stephanie B.

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Predictions of x-ray scattering spectra in warm dense matter

Charles Starrett (LANL)

Didier Saumon (LANL)
Andre Souza (U. Mich.)
David Perkins (UC, LA)
Stephanie Hansen (Sandia)

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Overview

- Introduction to our model of warm dense matter
- How x-ray scattering spectra are calculated from it
- Comparisons with experiments:
  - Room temperature/pressure beryllium
  - Warm dense beryllium
  - Warm dense aluminum
- Predictions for warm dense beryllium and titanium
- Conclusions

Model for warm and hot dense matter

Electronic structure:

- e^- density calculated assuming superposition approximation:

$$n_e(\vec{r}) = \sum_i n_e^{PA}\left(\left|\vec{r} - \vec{R}_i\right|\right)$$

- Pseudo-atom electron density:
  - Calculated in spherical symmetry (inexpensive)
  - Average atom type approach
  - Kohn-Sham - DTF

C.E. Starrett *et al*, HEDP (2014)

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Model for warm and hot dense matter

Ionic structure:

- Calculated with quantum Ornstein-Zernike relations
  Exact integral equations for fluid structure

- 3 closure relations are needed → approximations:
  Ion-ion: VMHNC
  Electron-electron: local field corrections
  Ion-electron: from pseudo-atom electron density.

C.E. Starrett *et al*, HEDP (2014)

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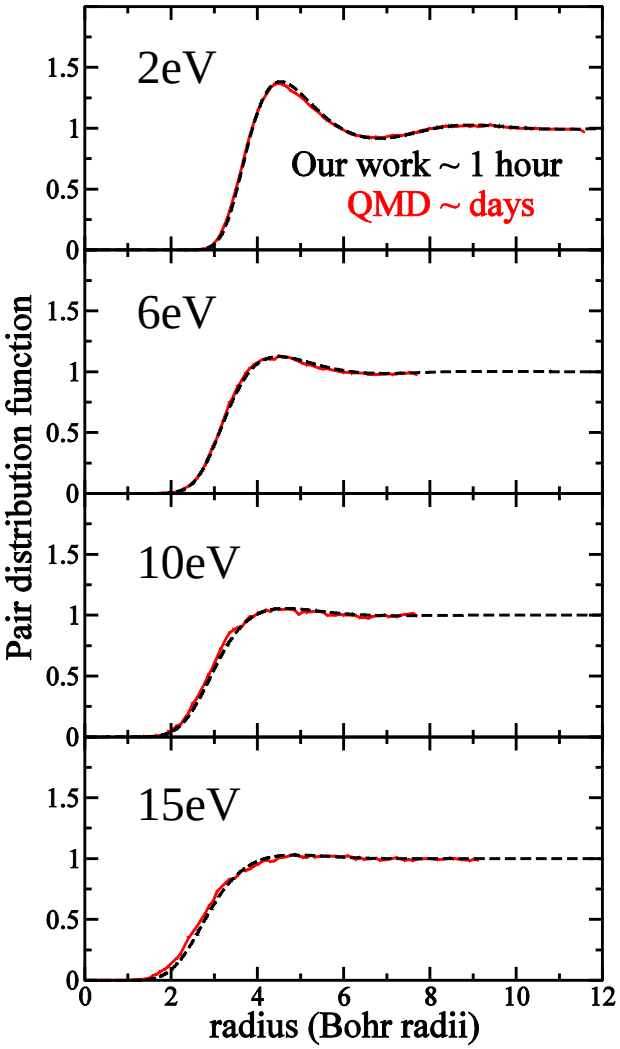
Comparison for warm dense aluminum

Example:
Ion-ion pair distribution functions for aluminum

Solid density (2.7g/cm^3)

Good agreement, much quicker!



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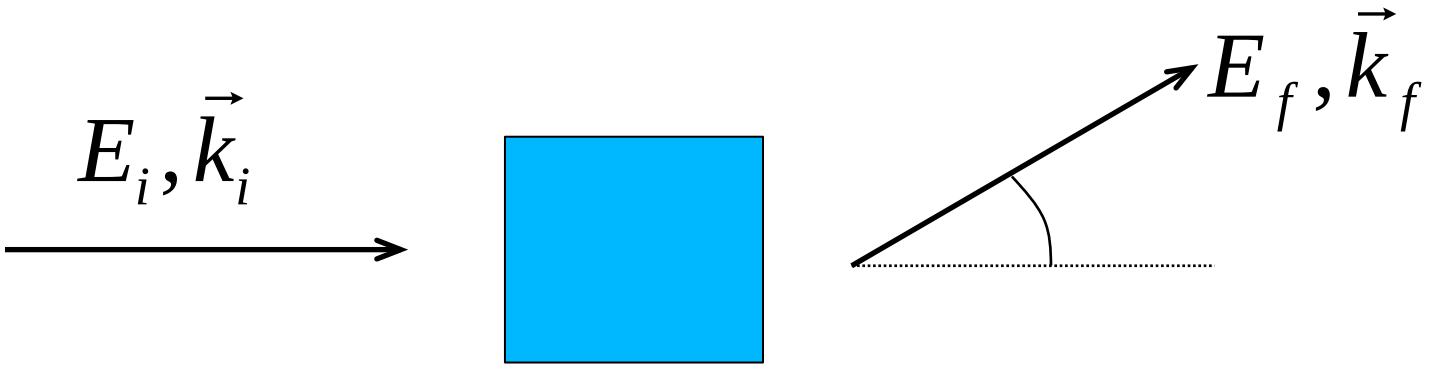
X-ray scattering



$$\hbar\omega = E_f - E_i$$ Energy transfer

$$k = \left|\vec{k}_f - \vec{k}_i\right|$$ Momentum transfer

Scattering is described by the dynamical structure factor

$$S(k, \omega)$$

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Calculating x-ray spectra

- We use the Chihara formula
  - Based on chemical picture
  - Relies on clear separation between bound and screening (valence) electrons
  - Suitable for simple fluids (eg. no bonding)

$$S(k,\omega) = \left| f_I(k) + q(k) \right|^2 S_{ii}(k,\omega) \quad \leftarrow \text{elastic}$$

$$+ \overline{Z}\, S_{ee}(k,\omega) \quad \leftarrow \text{free-free}$$

$$+ S_{bf}(k,\omega) \quad \leftarrow \text{bound-free}$$

Calculating x-ray spectra

Elastic feature:

$$\left| f_I(k) + q(k) \right|^2 S_{ii}(k, \omega)$$

$f_I(k)$ Fourier transform of bound electron density

$q(k)$ Fourier transform of screening electron density

$$f_I(r) + q(r) = n_e^{PA}(r)$$

We already calculate this in our model!

A.N. Souza *et al*, PRE (2014)

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Calculating x-ray spectra

Elastic feature:

$$\left| f_I(k) + q(k) \right|^2 S_{ii}(k,\omega)$$

$$S_{ii}(k,\omega) \approx S_{ii}(k)\delta(\omega)$$

Width of ion feature of the order ~ meV, width of x-ray probe ~ eV, so this is reasonable.

$S_{ii}(k)$ Already calculated in our model!

$S_{ii}(\omega,k)$ We plan to calculate this directly with MD

A.N. Souza *et al*, PRE (2014)

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Calculating x-ray spectra

Free-free feature

$$\overline{Z}\, S_{ee}(k,\omega)$$

Random phase approximation (RPA)

Collisionless approximation – questionable!

Needs, free electron density, ion density, and temperature as inputs (calculated in our model)

Born-Mermin (BM)

Includes electron-ion collisions (perturbative)

Also needs ionic structure factor and interaction potential (also calculated in our model)

A.N. Souza *et al*, PRE (2014)

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Calculating x-ray spectra

Bound-free feature

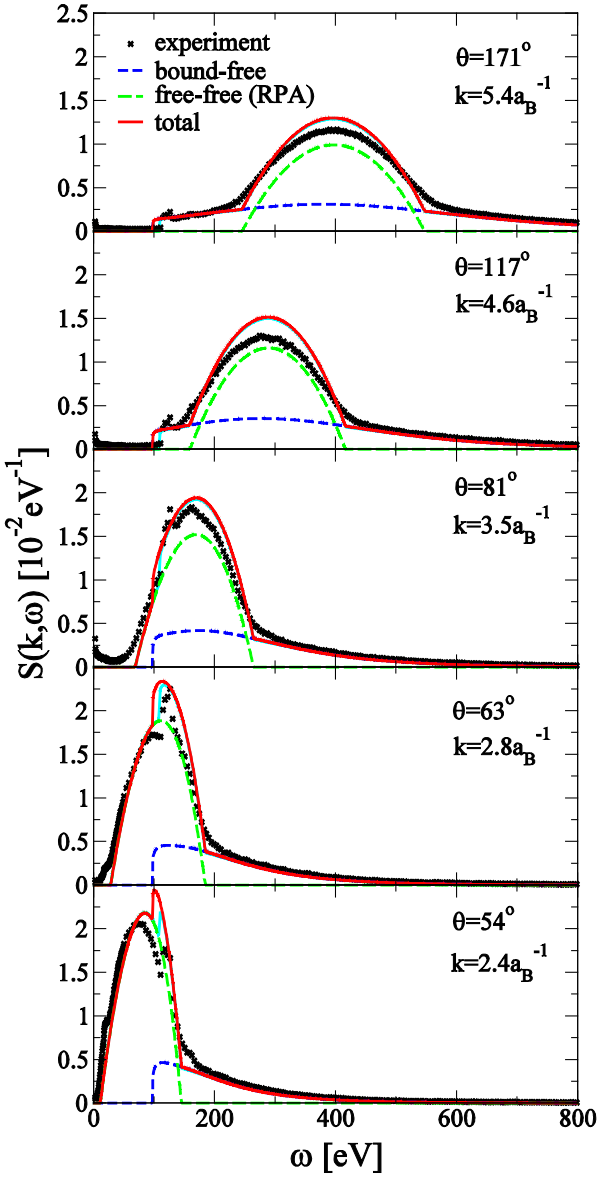
$$S_{bf}(k,\omega)$$

Calculate bound-free matrix elements using wave-functions from model (bound and free)

DFT wave-functions and eigenvalues – band gap problem!

W. Johnson *et al*, PRE (2012)

Validation on cold (solid) beryllium



Mattern *et al*, PRB (2012)

$$E_f = 9890eV$$

$$FWHM = 1.3eV$$

Free-free (RPA): too narrow, too strongly peaked

Bound-free: edge shifted, otherwise ok, tail in good agreement

Overall, reasonable agreement given ours is a plasma model

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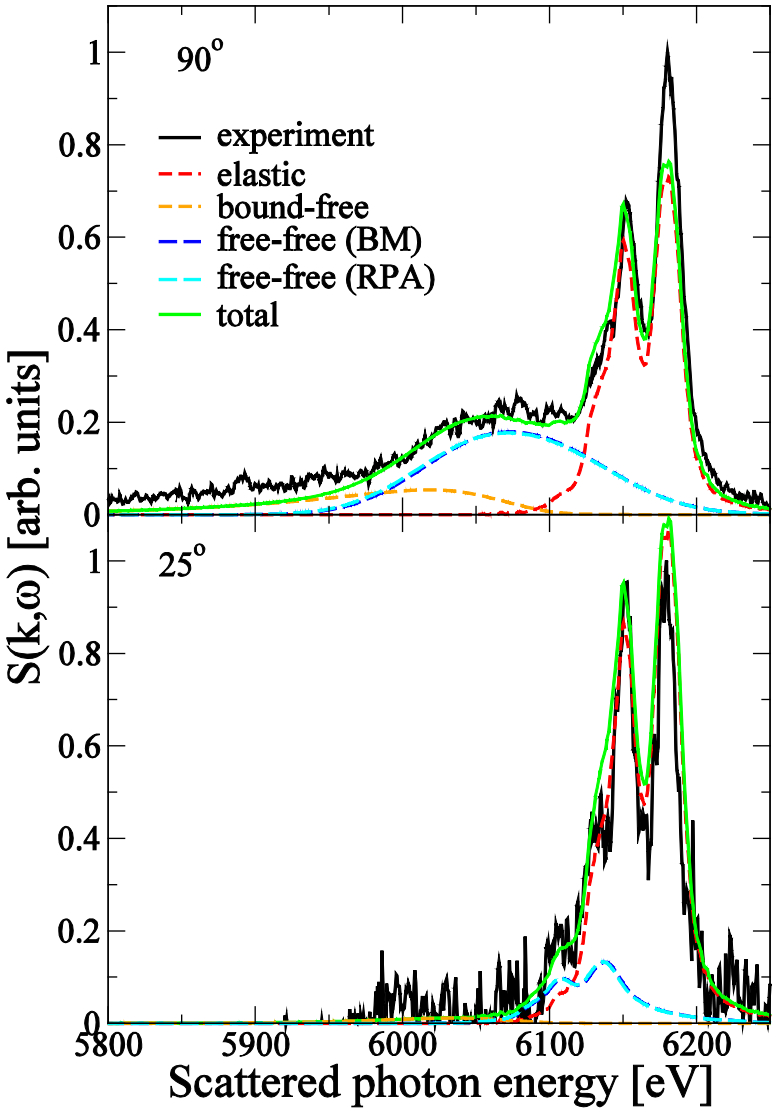
Warm dense beryllium: Normalization



HJ Lee *et al*, PRL (2009)

$$E_i \approx 6200eV$$

Mn He-α source

13eV

$3\rho_o = 5.55 g/cm^3$

Arbitrary normalization

90° Scattered spectrum incompatible with source!

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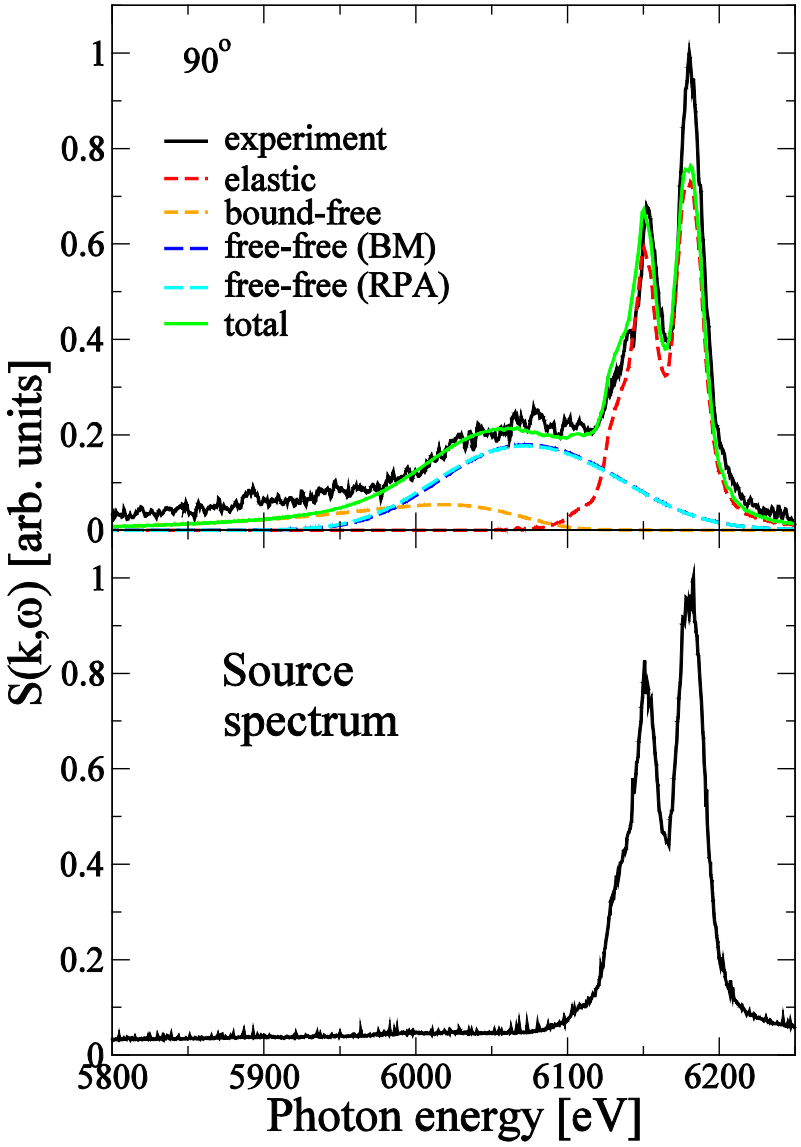
Warm dense beryllium: Components



HJ Lee *et al*, PRL (2009)

Inelastic components are shifted to lower energies compared to probe energy

Increase left-hand peak relative to right-hand
→Opposite to what is observed!

This implies variability in the probe beam

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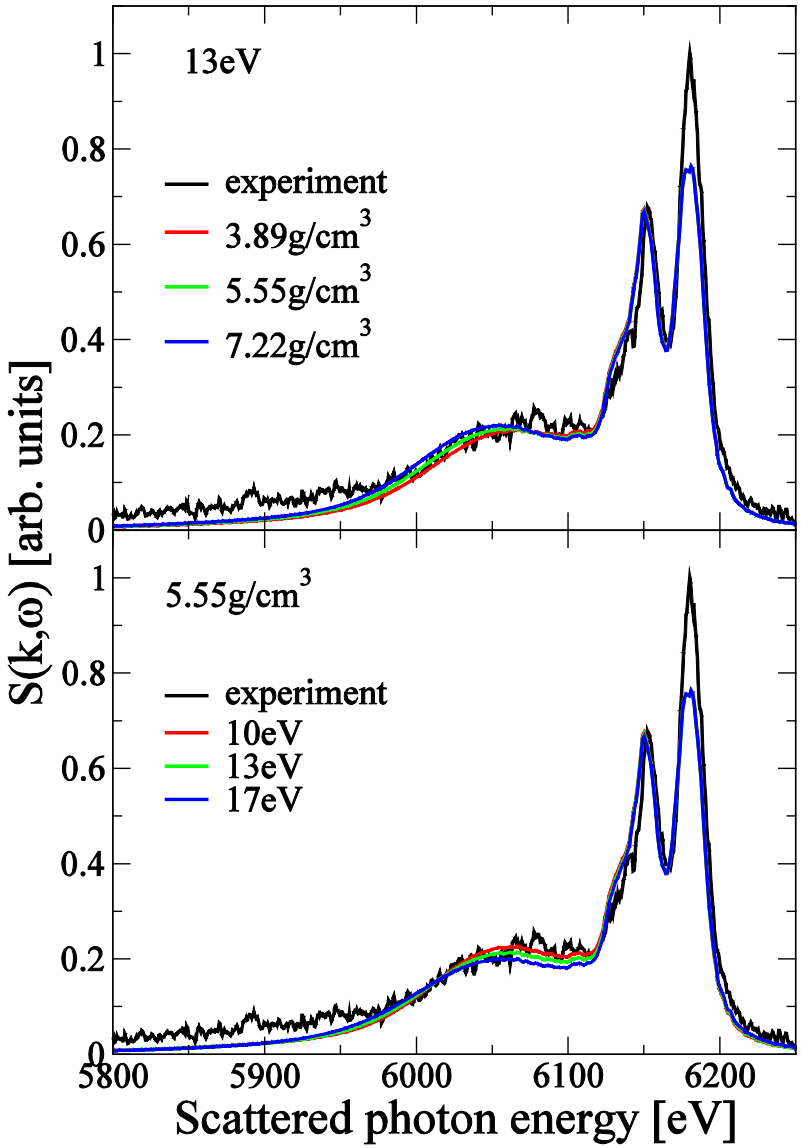
Warm dense beryllium: Sensitivity



HJ Lee *et al*, PRL (2009)

± 30% in temperature or density

Arguable that all curves fit data well, especially given source variability and arbitrary normalization

→Large error bars on density and temperature from fit.
→Uncertainty too large to constrain models

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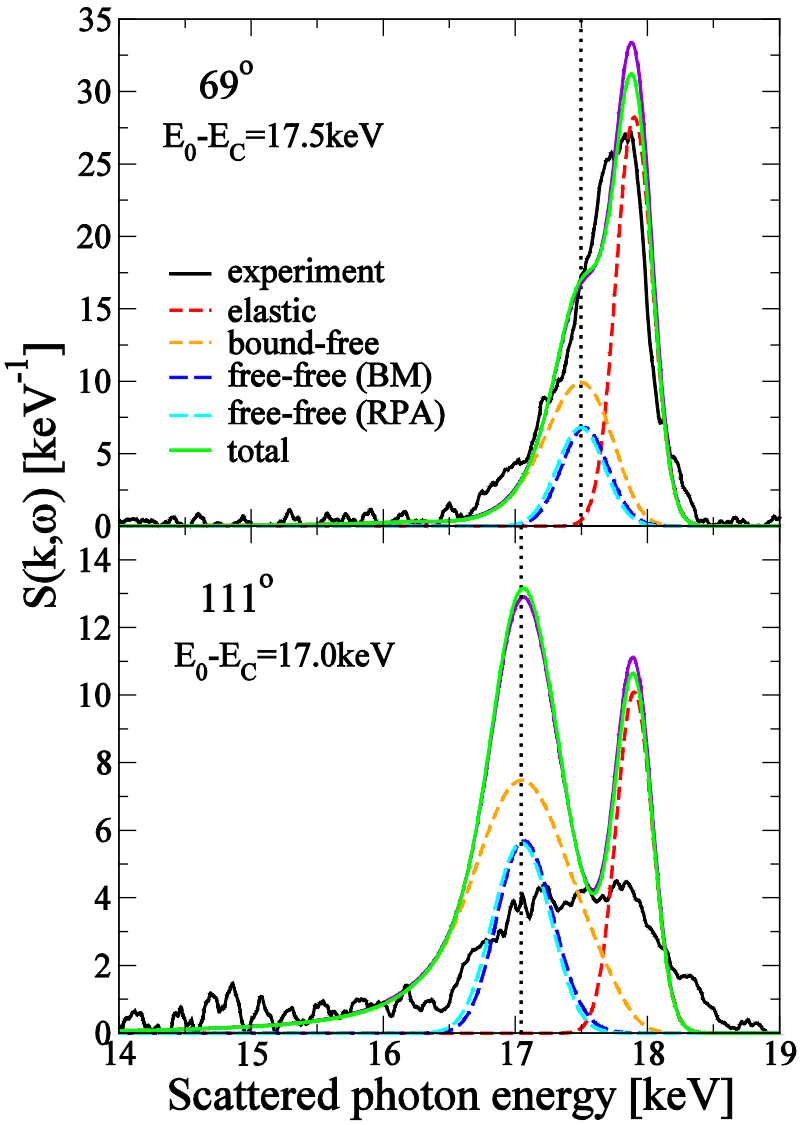
Warm dense aluminum



T. Ma *et al*, PRL (2013)

$$E_i \approx 17900eV$$

Mo 2p→1s source:
325eV FWHM Gaussian

10eV
$3\rho_o = 8.1 g/cm^3$

Absolute measurements

Good agreement at 69°
Strong disagreement at 111°

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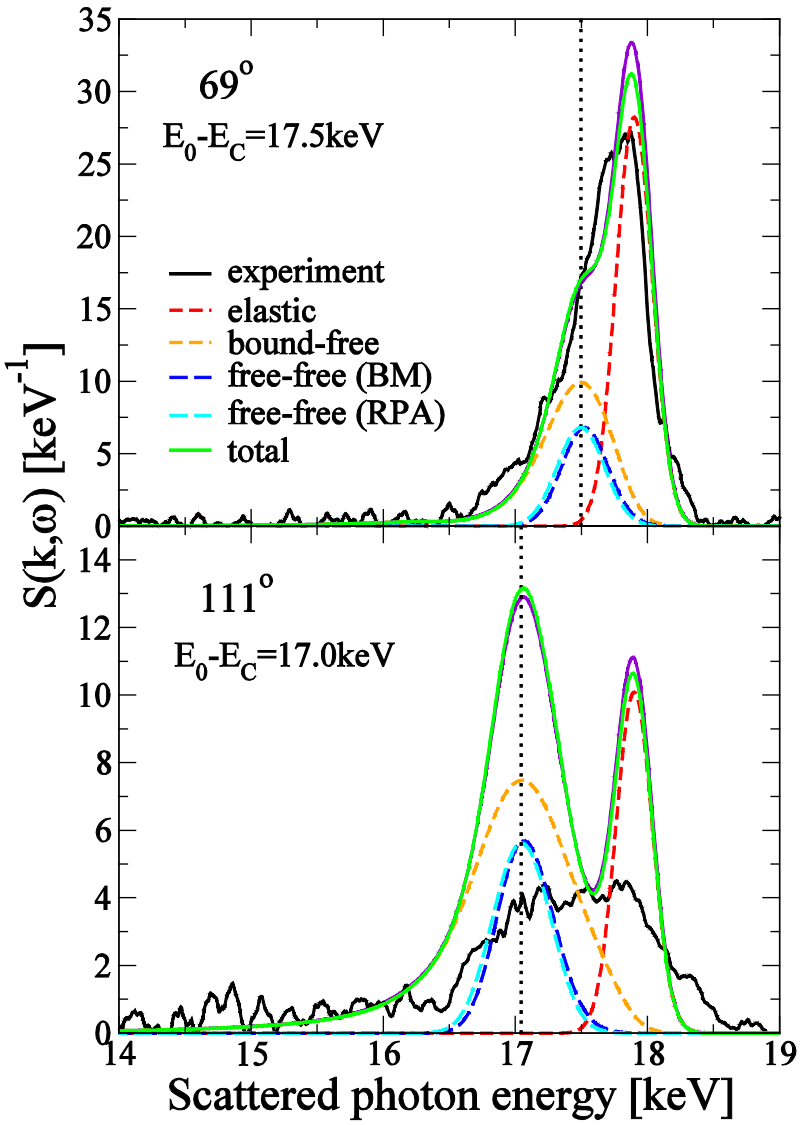
Warm dense aluminum



We checked:

- bound-free: compared to independent calculation (MUZE)
- Bound states against Dirac-Fock-Slater calculation
- Normalization vs. sum rules
- Exchange correlation potential
- $S_{ii}(k)$ vs. QMD
- RPA with 2 independent codes
- Validity of RPA
- Sensitivity to density and temperature (± 30%)
- Chihara model assumptions

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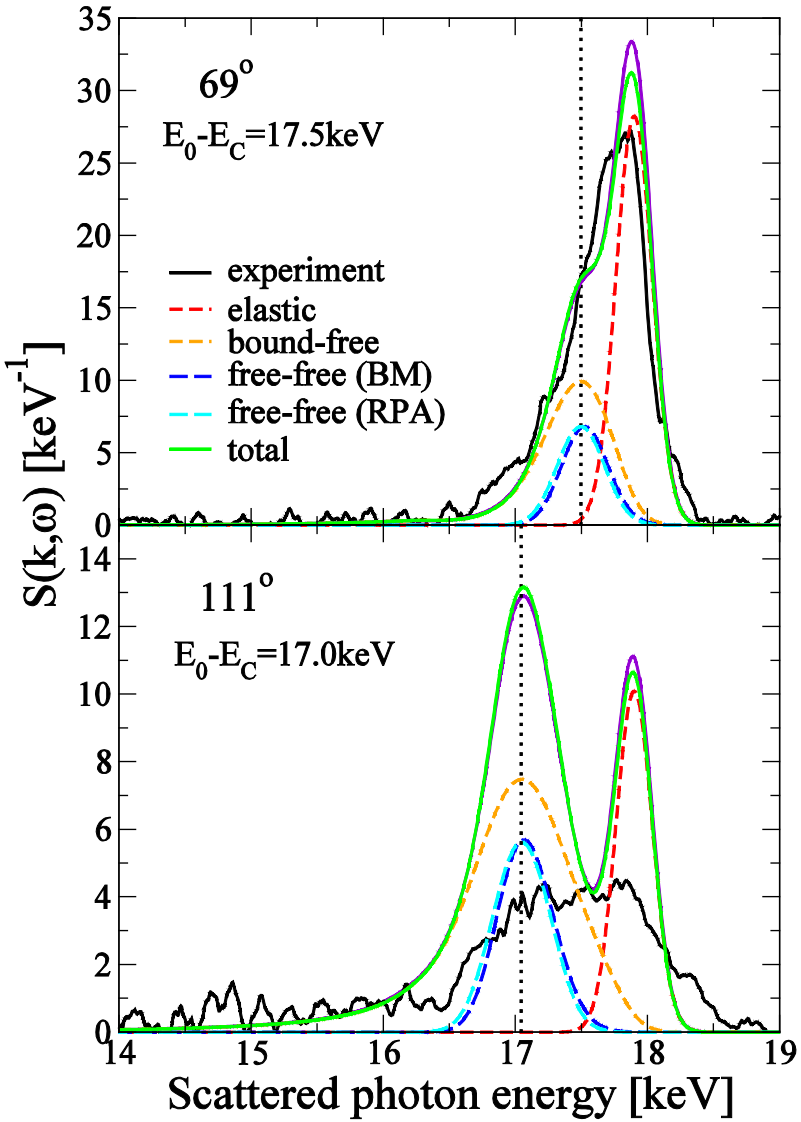
Warm dense aluminum



Conclusion:
→ Data at 111° cannot be reconciled with our model

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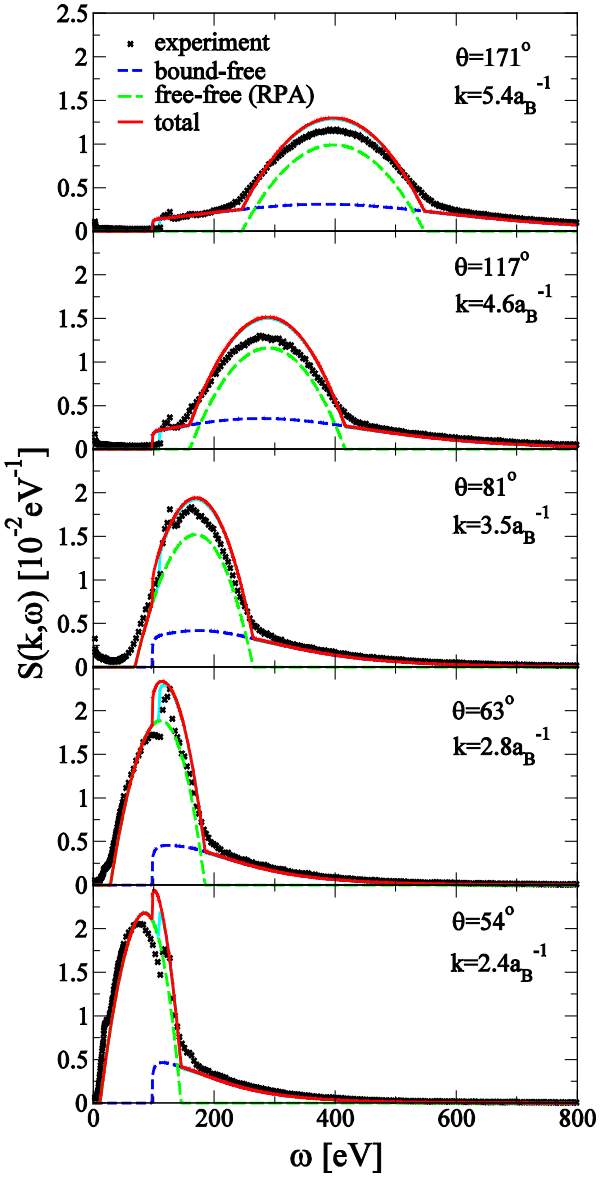
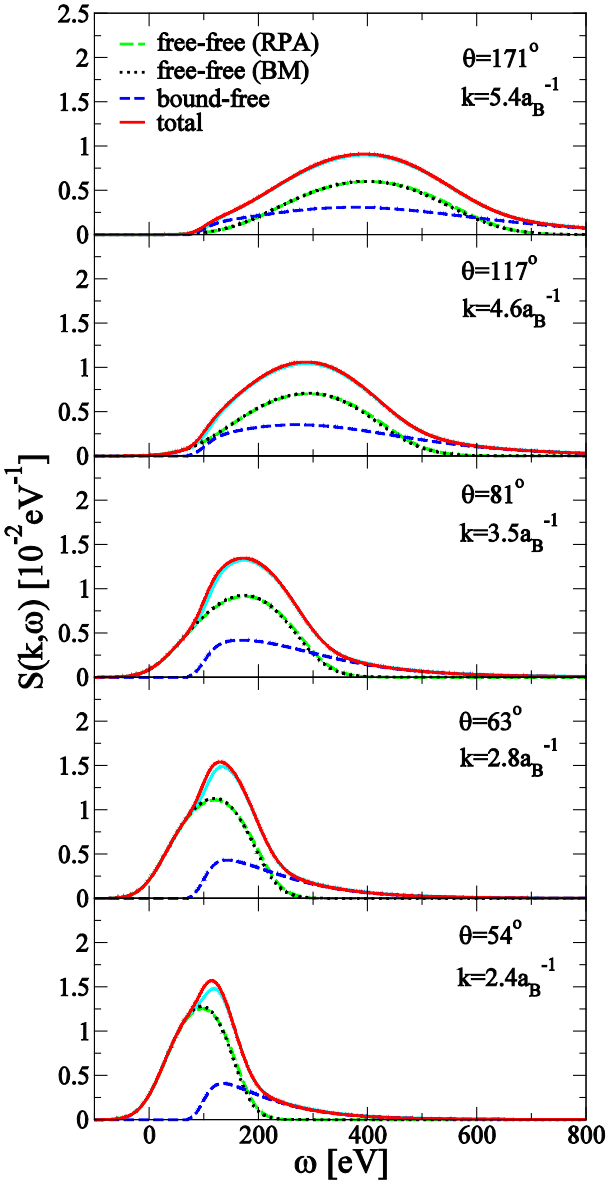
Hypothetical experiment on WD beryllium





$$E_f = 9890eV$$

$$FWHM = 1.3eV$$

13eV

$3\rho_o = 5.55 g/cm^3$

Temperature affect: Blurring of Fermi-edge

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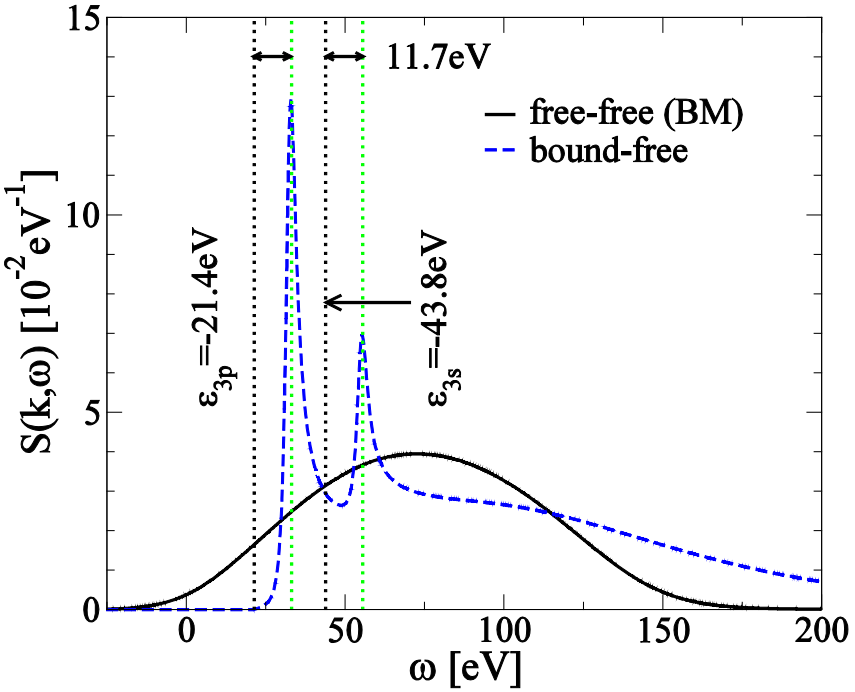
Resonances in warm dense titanium



$$E_i = 4750keV$$

Mono-energetic source

5eV
4.51g/cm^3
Angle: 130^o

Average atom predicts resonance structures that are expected to be too sharp, due to spherical symmetry

Source spectrum would need to be narrow (~few eV) to measure width of feature

Chihara formula assumptions may break down

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Next steps for theory

- Improve free-free calculation. RPA and BM questionable for WDM – could use wave functions or density of states to improve free-free

- Beyond the Chihara formula

However, the theory has not yet been proved inadequate by experiment!

Conclusions

• We have seen little sensitivity in density and temperature for experiments on Be and Al

→ May be greater sensitivity in other thermodynamic regimes

• Ability of experiments to test models hindered by source variability and large energy width of source spectrum

• Chihara formula must be used with caution – assumptions not valid at or near pressure ionization, or where binding is significant

In an ideal world…

For a probe beam width < 5eV we could look at:

- Bound state → resonance transitions
- Broadening of bound-free edge due to smearing out of bound states into bands
- Is the RPA good enough for free-free?
- Bound state energies vs. DFT energies
- Break-down of Chihara formula near pressure ionization?

In short, we could probe the microscopic physics of warm dense matter and see how well (or poorly!) the models do

Acknowledgements

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  Didier Saumon (LANL)

  Andre Souza (U. Mich.)

  David Andre (UC, LA)

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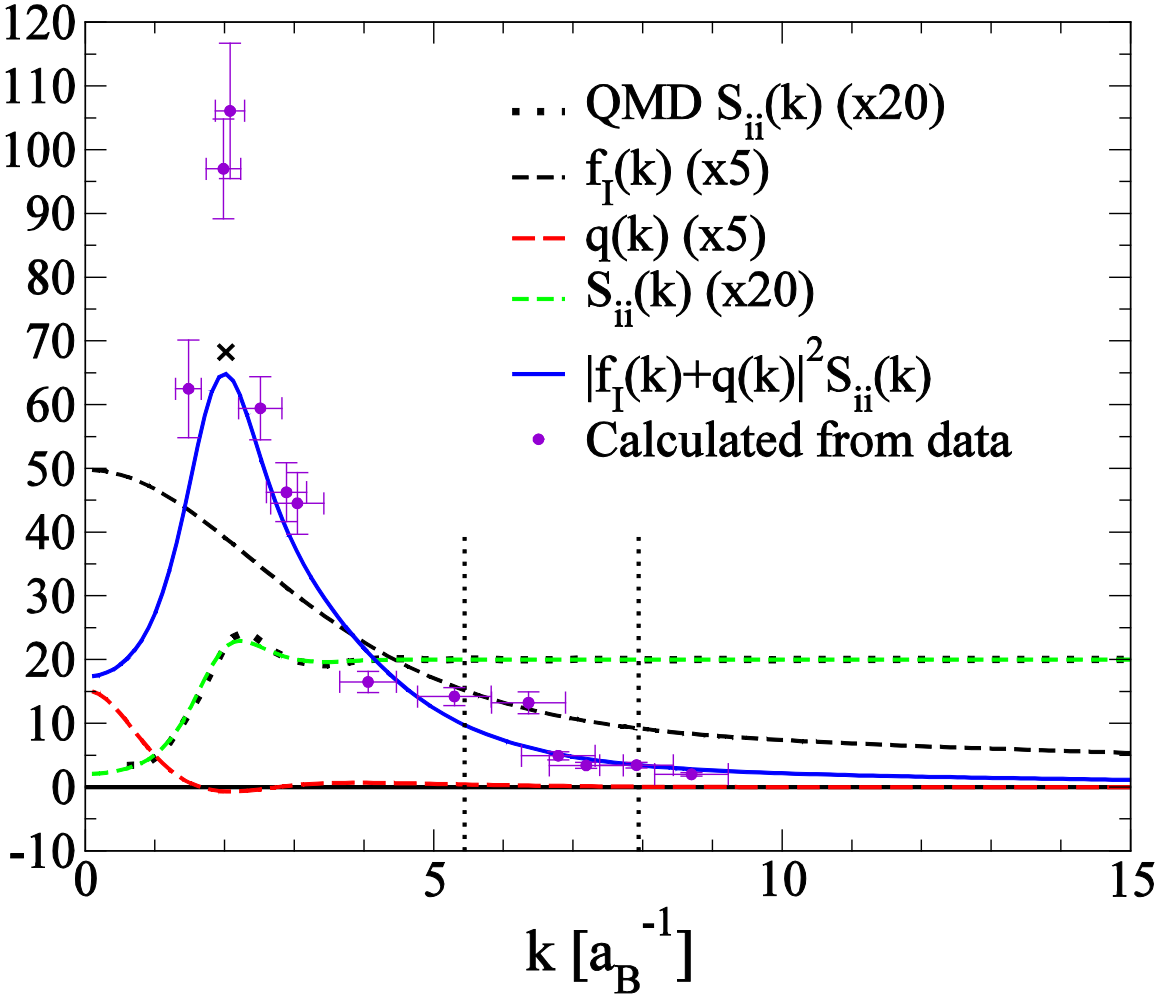
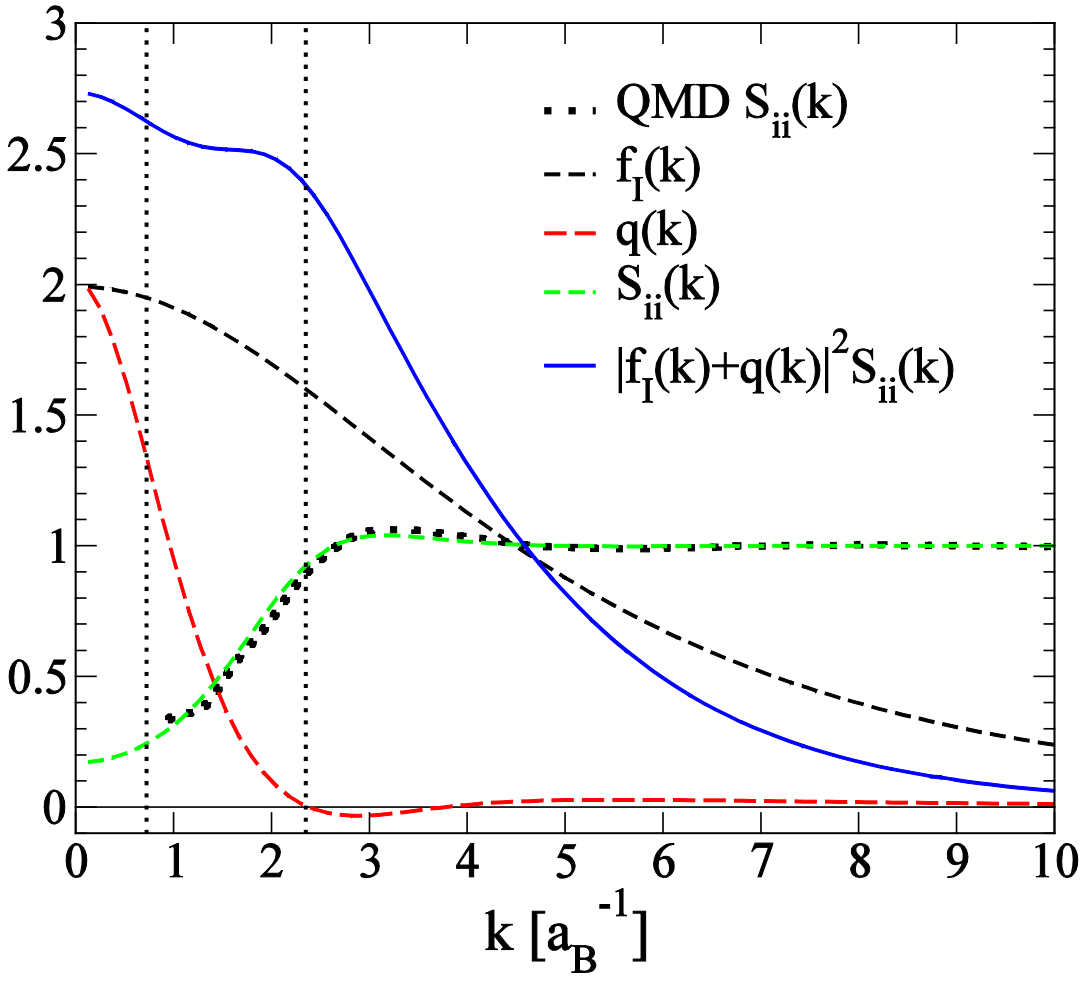
Backup slides: aluminum elastic feature



Backup slides: WD beryllium elastic feature



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